

Repeatability and Reproducibility of Field Exposure Results

by

Jonathan W. Martin
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

Reprinted from the Service Life Prediction: Methodology and Metrologies, American Chemical Society Symposium Series 805, Jonathan W. Martin, David R. Bauer, eds., pp. 2-22, 2002.

NOTE: **This paper is a contribution of the National Institute of Standards and Technology and is not subject to copyright.**



National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Chapter 1

Repeatability and Reproducibility of Field Exposure Results

Jonathan W. Martin

National Institute of Standards and Technology, 100 Bureau Drive, Stop 8621,
Gaithersburg, MD 20899-8621

Field exposure results are almost always viewed as the de facto standard of performance against which laboratory results must match in estimating the service life performance of polymeric materials. Implicit in this view is that field exposure results are both repeatable and reproducible. A review of the literature was made in to identify evidence corroborating or refuting this premise. It was concluded from this review that substantial evidence exists refuting this premise and, correspondingly, little or no evidence exists supporting it; that is, the assumption that field exposure results are repeatable or reproducible does not appear to have any scientific merit. This lack of support draws into question the use of field exposure results as a de facto standard of performance. Alternative strategies are noted.

Introduction

Field exposure experiments play a crucial role in assessing the in-service performance of coatings and other polymeric materials. Results from these experiments are viewed as the “primary test” [1], the “real time exposure” [2-4], the “decisive test” [5], and thus the de facto standard of performance against which laboratory aging and fundamental mechanistic results are expected to match. Since field exposure results are viewed as a performance standard, these results should be expected to be both repeatable and reproducible. No support, however, could be found in the literature either corroborating or refuting these premises. The objective of this paper, therefore, was to review the published literature for such evidence.

Three sources of information were examined. They included the following:

- testimonials from weathering researchers,
- 2. results from well-designed and executed field exposure experiments, and
- 3. trends and cycles in weather element data.

Representative citations from each source are presented; a more in-depth presentation and a more comprehensive list of citations are given in Martin [6].

Testimonials

Over the years, many weathering researchers have published testimonials on the reproducibility and repeatability of field exposure experiments. Unfortunately, few of these researchers provided any quantitative data to support their statements. The testimonials generally deal with the effect of different variables on weathering results. These variables include 1) the year of exposure, 2) the time of year that the exposure commenced, 3) the duration of the exposure, 4) the angle of the exposure, and 5) the location of the exposure site. The consensus of opinion is that field exposure results are neither repeatable nor reproducible when specimens are exposed

- at the same site, at the same angle of exposure, at the same time of the year, and for the same duration, but exposures begin on **different years** [7-11];
2. at the same site, at the same angle of exposure, during the same year, for the same duration, but exposures begin at **different times of the same year** [1-2, 8-9, 12, 15-18];
3. at the same site, at the same angle of exposure, at the same time of the year, in the same year, but exposures are for **different durations** [19-22];
4. at the same site, at the same time of the year, in the same year, for the same duration, but exposures are made at **different exposure angles** [7, 14, 23-25];
5. at the same angle of exposure, at the same time of the year, in the same year, for the same duration, but exposures are at **different exposure sites** [1, 7, 9, 11-12, 18-23, 26-28].

The only citation found that contradicted the claim that field results are neither repeatable nor reproducible was by Dawson and Nutting [29].

Results from Well-Designed and Executed Field Exposure Experiments

From 1900 through 1970, a number of planned field exposure experiments were conducted and the results published in the open literature. In a few cases, the experiments included several thousands of specimens exposed over a number of years. By the end of the 1970's, however, the philosophy of field exposure experimental designs changed rather dramatically. Instead of designed experiments yielding vast amounts of quantitative data, field experiments were designed to make a simple comparison between two or more exposures. The degree of agreement between or among these exposures was assessed through a correlation coefficient, usually the Spearman rank correlation coefficient. Although these experiments are much easier

to design and execute, almost all quantitative data, like “how much is coating A better than coating B”, have been lost [6]. Since the purpose of this section is to quantitatively assess the repeatability and reproducibility of field exposure results, only results from well-designed experiments published prior to 1980 are described. They include the following:

- a. Oakley [8] exposed nominally identical coated panels at the Carlton Exposure Station in County Durham, England over a three-year period starting in 1957. The experiments were terminated after 36 weeks at which time the gloss loss of each panel was assessed. He concluded that panels exposed in 1959 exhibited about 15% greater gloss loss than did panels exposed in 1958 which, in turn, exhibited about 15% greater gloss loss than panels exposed in 1957.
- b. Mitton and Church [10] exposed nominally identical coatings in Miami, FL at different times from 1948 to 1953. They reported that the results were highly variable and that the majority of this variability was attributable to variations in the weather.
Ramsbottom [13] exposed fabrics, used in the construction of dirigibles, in Farnborough, England starting on July 1, 1922 and the beginning of each month thereafter until July 1, 1923. The fabrics were exposed for one month; at the end of which, the fabrics were removed from exposure and failed in tension. Tensile strength loss of the fabrics ranged from 0% for fabrics exposed during November 1922 to 45% for fabrics exposed during July 1923. Ramsbottom concluded that summer exposures were more severe than winter exposures.
- d. Came [30] exposed two nominally identical sets of 50 spar varnishes at the National Bureau of Standards in Washington D.C. on two different start dates: January 10, 1929 and April 1, 1929. Exposures continued until almost all of the varnishes had failed. Came recorded the time to failure for each varnish and observed that specimens placed on exposure in January failed about twice as fast as did specimens that were exposed starting in April, 1929.
- e. Wirshing [15] initiated exposures of nominally identical sets of nitrocellulose coated panels on successive months during the same year and removed the panels from exposure whenever a fixed amount of degradation was observed. He observed that panels exposed at the beginning of April, May and June failed in 13 weeks, whereas panels exposed at the beginning of November took 21 weeks to fail. Thus, panels having spring or summer exposure start dates degraded much faster than panels having a winter start date. This observation is in direct opposition to that made by Came [30].
- f. Clark [1] exposed a series of vinyl films in Miami, FL and Bound Brook, NJ at the beginning of the spring, summer, fall and winter seasons. Exposures were continued for two years. Clark concluded that films having exposure start dates from May to August (summer) degraded about three times faster than did films having start dates from November to March (winter and spring). That is, summer start dates were more severe than winter start dates.

- g. Melchore [16] initiated exposures of polyethylene films in Arizona at the beginning of each month for a year. The experiments were terminated whenever the total solar irradiance absorbed by a specimen reached 15000 Langleys at which time the percent carbonyl formation in the film was determined. Melchore observed that, even though all of the films absorbed the same number of Langleys, films placed on exposure in June and July degraded 7 times faster than those exposed in December and January. He concluded, "the Langley is a poor unit to measure ultraviolet radiation" and that films having a summer start date degraded much faster than films having a winter start date.
- h. The Joint Services Research and Development Committee on Paints and Varnishes [17] exposed a variety of coatings in six different locations throughout England for approximately two years starting in the fall of 1959 and the spring of 1960. They observed that the degradation rate for the spring exposure was much greater than the rate for fall exposure. Marshall et al. [23] exposed several thousands of coated panels in Miami, FL, Wilmington, DE, and Canyon, TX at 45° S and 90° S (i.e., vertical South) for 36 months in the early 1930s. The dominant failure mode was flaking. For all three-exposure sites, the rate of flaking was more severe for panels exposed at 45° S than it was for panels exposed at 90° S. Evans [25] exposed pinewood panels (*Pinus radiata*) at 0° (horizontal), 45°, 60°, 70°, and 90° (vertical) for 50 days in Canberra, Australia (latitude 35° South) from February 18, 1987 to April 9, 1987 and monitored mass loss and chemical changes. Panels positioned horizontal to the sun experienced the greatest mass loss and the greatest chemical change.
- k. Qayyum and Davis [24] exposed polysulphone films at 0° (horizontal), 20°, 45°, 60°, and 90° (vertical) South in Jeddah, Saudi Arabia (latitude 20° North) for a 12-month period starting in September 1981. Degradation was monitored by mass loss. They observed that mass loss was negatively correlated with total solar UV-irradiation; that is, the greater the total solar UV-irradiance, the lower the mass loss. Maximum mass loss was observed on films exposed vertically, 90° S, while minimum mass loss was observed for films exposed horizontally, 0°. This conclusion is in opposition to those made by both Marshall et al. [23] and Evans [25]. Marshall et al. [23] exposed several thousand coated panels in Miami, FL, Wilmington, DE, and Canyon, TX in the early 1930s. The exposures were terminated after 36 months, at which time, the amount of flaking was ascertained. They observed that the degradation response varied greatly among the three sites and concluded that knowledge of the time-to-flaking at one or even two of the exposure sites would not provide any useful information regarding the time-to-flaking at the third site. Neville [26] exposed acrylic and alkyd coated panels in Carlton, County Durham, England and Miami, FL. Changes in gloss were reported as a function of total solar irradiance. Neville concluded that total solar irradiance was not a good metric for predicting gloss loss, since for the same

total solar irradiance, gloss loss in Florida was much greater than it was in Carlton.

- n. The Joint Services Research and Development Committee on Paints and Varnishes [17] exposed a number of coatings at six different locations throughout England for approximately two years. They observed that both the rate of weathering and the dominant failure mode changed from site-to-site.
- o. Cutrone and Moulton [28] exposed nominally identical sets of coated specimens at 11 different field sites throughout the world during the same year. The computed Spearman rank correlation coefficients [31] ranged from 0 to 0.8. The authors concluded, "the results indicate another less-than-perfect correlation."

The results from planned field experiments quantitatively affirm the testimonials; that is, field exposure experiments are neither repeatable nor reproducible. For example, for exposures begun on contiguous years, results can vary by as much as a factor of 10. No planned experiment was found in the literature supporting the premise that field exposure results are either reproducible or repeatable.

Trends and Cycles in Weather Element Data

The weather and, thus, the elements of the weather influence weathering results. In weathering research, the weather elements of primary research interest are solar ultraviolet (UV) radiation, air surface temperature, relative humidity, precipitation and aerosols. In this section, the temporal and spatial stabilities of these weather elements are reviewed for trends and cyclic behavior.

Over the last hundred years, meteorologists have performed numerous and extensive statistical analyses aimed at determining the temporal and spatial stability of a wide variety of weather elements. Temporal stability is ascertained by determining if trends and cycles exist in the time series for each weather element. Spatial stability is assessed by aggregating the time series output from various subset of the meteorological network at different geographical scales and determining if the trends and cycles translate from one spatial to another.

A trend is present in a weather element time series if the moving average for the time series (usually the five or ten year moving average) is increasing, decreasing, or is level over some period of time (Figure 1). Cyclic behavior is discovered through the application of spectral analysis techniques, like Fourier analysis, to a time series. The presence of a cycle implies that the intensity of a weather element repeats over some time period (Figure 2). In the meteorological literature, a cycle is considered to be statistically significant whenever the spectral peak for this cycle explains at least 5% of the total variation in a weather element's behavior. For practical reasons, weathering cycles between 2 and 5 years are of particular interest in materials research, since this is the length of time that specimens are commonly exposed in the

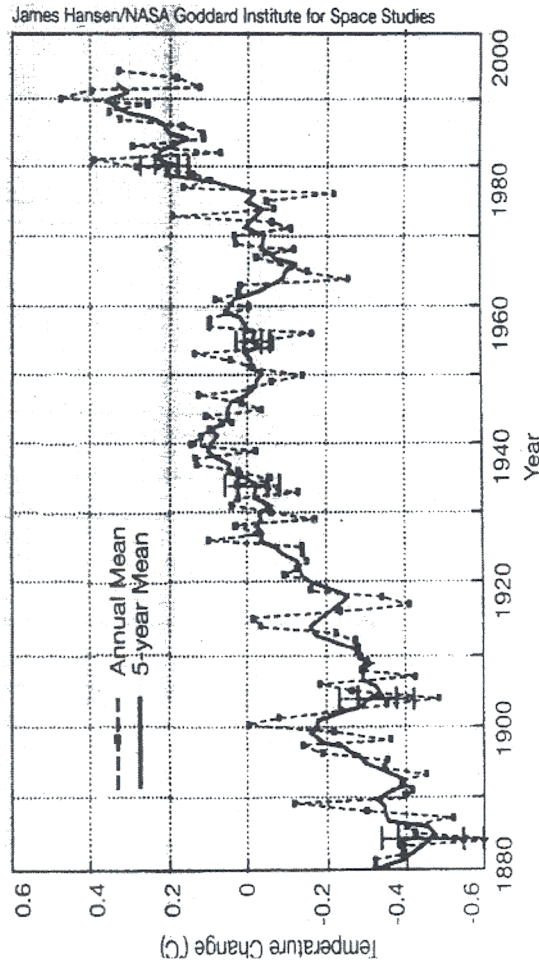


Figure 1. Global air-surface temperature, annual and 5-year-moving-average, from 1880 to the present.

field. Thus, the trend and cycle characteristics of a weather element that would tend to support repeatable and reproducible weathering results are those in which the trend line for a weather element displays a zero-slope and spectral analysis of the time series data indicates several statistically significant cycles between two and five years. Conversely, trend and cycle characteristics for a weather element, that would not tend to support repeatable and reproducible weathering results, include those in which the trend line for this weather element is either an increasing or decreasing and spectral analysis of the time series data indicates no statistically significant cycles between two and five years.

Spectral Ultraviolet Radiation

Radiation from the Sun provides essentially all of the energy driving the Earth's weather. Fortunately, solar radiation reaching the Earth's surface is greatly attenuated by the Earth's atmosphere. This is particularly true in the ultraviolet (UV) region, the radiation that is most photolytically effective in degrading materials. The Earth's stratospheric ozone layer, for example, effectively absorbs all solar ultraviolet radiation below about 290 nm. Solar ultraviolet radiation transmitted through the Earth's atmosphere between 290 and 400 nm is known to be photolytically active in degrading polymeric materials. The photolytic effectiveness, however, varies greatly with wavelength. Wavelengths closer to 290 nm may be three to seven orders of magnitude more photolytically effective than are wavelengths near 400 nm. Photolytic effectiveness of radiation is not limited to the ultraviolet region. For some materials, like paper, wavelengths as high as 550 nm are known to cause photodegradation [32]. Thus, a full characterization of the solar spectral radiation between 290 nm and, let's say, 550 nm may be required to fully characterize the photodegradation effects of solar radiation.

Meteorological stations for monitoring solar spectral ultraviolet radiation are a recent phenomena [33,34]. Weatherhead and Webb, for example, reported that the global solar spectral UV monitoring network consisted of five stations in 1992 and 250 stations in 1998. In the US, funding for most of these stations has been provided by the Departments of Energy, Agriculture, Commerce, Environmental Protection Agency, and the National Science Foundation under the auspices of the US Global Climate Change Research Program [35]. With two exceptions, the time series from this network are shorter than the 11 year solar cycle. The two exceptions are a worldwide network of Robertson-Berger (R-B) meters [36] and a filter wheel radiometer station located in Rockville, MD and operated by the Smithsonian Environmental Research Center (SERC) [37].

The Robertson-Berger meter is a broadband radiometer equipped with a filter that selectively transmits radiation approximating the erythral absorption spectrum. The radiation transmitted through the filter is reported in terms of sunburn units. For 2 six-year periods starting in 1974 and again in 1980, the medical community instrumented 27 cities throughout the world with these instruments and correlated their output against the incidence of melanoma and non-melanoma cancers [36]. The usefulness of this meter for materials research, however, is limited since the exposure

metric is tailored to the erythral spectrum which is not useful absorption or quantum yield spectrum for commercial polymeric materials.

The SERC radiometer contains a filter wheel with 18 2nm-nominal band pass interference filters on its periphery and is equipped with a R-1657 solar blind photomultiplier tube detector. The photomultiplier tube is temperature regulated via a thermoelectric system. The filter wheel turns at 15 revolutions per minute and contains 18 2nm full width half-maximum interference filters with nominal center wavelengths from 290nm through 324nm. Data from each interference filter is averaged over a 12 minute interval and this averaged value is stored in a computer as a observation in the time series for this filter. The unit operates 24 hours a day and is calibrated three or four times per year using NIST traceable calibration protocols. One unit has been in continuous operation in Rockville, MD or its vicinity since 1975; and, since 1998, similar units have been in operation in Miami, FL and Phoenix, AZ. Correll et al. [37] plotted erythema dosage (a unit of measure similar to sunburn units) for this unit from 1975 through 1990. For the Rockville, MD site (see Figure 3), erythema dosage decreased 14% from 1975 through 1981; increased 40% from 1981 through 1987; and decreased 9% from 1987 through 1990. According to the authors these changes are consistent with TOMS satellite data and with changes in the total ozone column thickness recorded during these periods. The spectral UV trends observed by SERC are also consistent with short-term trends observed by other researchers; see, for example, McKenzie [38] and Kerr and McElroy [39]. To date, no spectral analysis research has been found for any solar spectral UV data.

Air-Surface Temperature

Time series for air-surface temperature are the longest and have the highest meteorological network station density for any weather element. The air-surface temperature time series for the British Isles, for example, dates back to 1659 [40]. Due to the length of the time series and the dense spatial distribution of monitoring stations, air-surface temperature time series are very attractive candidates for both trend and spectral analyses.

Representative air-surface temperature trends are presented in Table 2.1 over several geographical scales. For presentation purposes, these time series have been segmented into four independent time intervals: a) 1860 to 1900, b) 1900 to 1940, c) 1940 to 1975, and d) 1975 to the present. The trend in the air surface temperature for each time segment is indicated by one of the following arrows: 1) \uparrow for increasing temperature trend, 2) \downarrow for a decreasing temperature trend, and 3) \rightarrow for a zero-sloped trend.

From Table 2.1, less than 25% of time segments are best described as having a zero-sloped trend. The trends for the remaining time segments are either increasing or decreasing. Most of the zero-sloped trends occurred during the time period from 1860 to 1900. From "1900 to 1940" and from "1975 to the present", the air surface temperature trends for almost all geographical scales were increasing; while, from 1940 to 1975, the trends for almost all geographical scales were decreasing.

Weather cycles: real or imaginary?

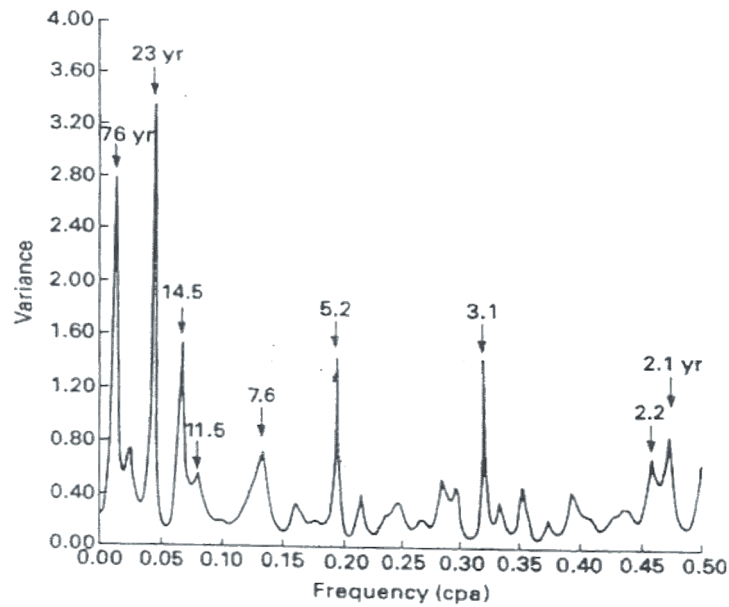


Figure 2. Typical spectral analysis output for a weather element. Spectral peaks 2. y, 5.1 y, and 20 y are statically significant at the 95% level (Fig. 2.taken from Spar and Mayer [67]).

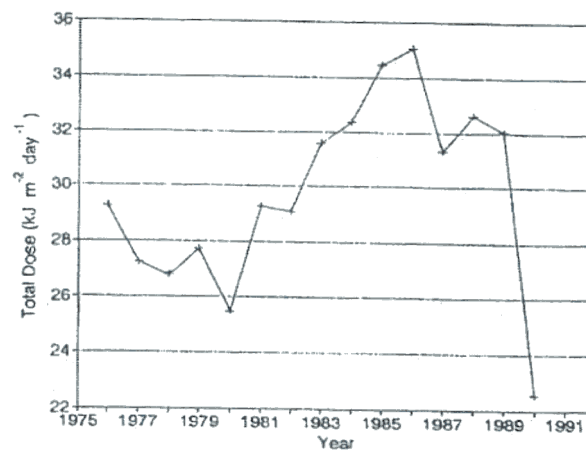


Figure 3. Smithsonian Environmental Research Center's Rockville, MD time series of annual mean daily total dosage of integrated 295-320 nm global irradiance [37]

TABLE I. Air-surface Temperature for Four Periods from 1860 to the Present at Decreasing Geographical Scales.						
<i>Spatial Scale</i>	<i>Author (year)</i>	<i>Trend 1860--1900</i>	<i>Trend 1900-1940</i>	<i>Trend 1940- 1975</i>	<i>Trend 1975- present</i>	
Global	Jones [59]	→	↑	→	↑	
Southern Hemisphere	Jones [59]	→	↑	↓	↑	
Northern Hemisphere	Jones [59]	↑	↑	↑	↑	
Eurasia	Diaz and Bradley [60]	→	↑	→	↑	
North America	Diaz and Bradley [60]	→	↑	↓	↑	
Continental US	Diaz and Bradley [60]	↓	↑	↓	↑	
Eastern US	Diaz and Bradley [60]	↓	↑	↓	↑	
Western US	Diaz and Bradley [60]	→	↑	→	↑	
Colorado and Platte River Basin	Diaz and Bradley [60]	→	↑	↓	↑	

Spectral analysis results for air surface temperature are tabulated in Table 2.2. Only time series of length longer than 50 years and statistically significant cycles having a cycle time longer than one year are included. From Table 2.2, few statistically significant cycles have been identified and even fewer cycles translate from one geographical scale to another.

In conclusion, neither trend analysis nor spectral analysis for air surface temperature time series provide support for the repeatability and reproducibility of weathering results regardless of the time scale or the geographical location.

Precipitation

Moisture degrades polymeric materials through hydrolysis and acts together with other weather elements in degrading materials. In the hydrosphere, moisture is stored in five reservoirs: 1) the oceans, 2) the ice masses and snow deposits, 3) terrestrial waters, 4) the atmosphere, and 5) the biosphere. Although each reservoir could degrade polymeric materials, discussion will be limited to atmospheric moisture, specifically, precipitation and relative humidity.

Precipitation and air-surface temperature time series data are almost always collected concurrently; thus, it is not surprising that, like air-surface temperature, the time series for precipitation are of great length and the density of the monitoring sites are closely packed. The longest instrumented time series for precipitation dates back to 1727 and it covers most of England and Wales. A longer precipitation time series starting in 1470 AD is available for China, but this time series is largely descriptive and is considered by some researchers to be unsuitable for predictive purposes [76].

From extensive spectral and trend analyses on numerous precipitation time series, meteorologists have concluded that both temporal and spatial variabilities for the precipitation time series are significantly greater than they are air surface temperature. Bradley [45] performed trend analyses for precipitation data from 1850 to 1973 for the Northern Hemisphere using data collected from 1410 stations. He concluded that the precipitation trends were 1) decreasing from 1870 to 1920, 2) increasing from 1920 to 1950, and 3) decreasing from 1950 to 1973. Hense [46] reported precipitation data for the Earth's Equatorial Regions from 1965 to 1984 and concluded that precipitation increased an average of 0.005 mm/y in the Indo Pacific Equatorial Regions and increased an average of 0.05 mm/y in the Americas and African Equatorial Regions. Groisman [47] performed trend analysis on precipitation for the former USSR from 1890 to 1990 and observed annual increases of 6% per year for all regions except one.

Spectral analysis results for precipitation are tabulated in Table 2.3. Spectral peaks around 3.9 years and around 10 years appear in several time series, but these cycles do not translate from one geographical scale to another.

Relative Humidity

Atmospheric moisture may be a greater contributor to weathering than precipitation. Most atmospheric relative humidity data are obtained from radiosondes or rawinsondes, that is, vertical ascending instrumented balloons used in monitoring atmospheric climatic variables. Currently, radiosondes are launched twice daily from

TABLE II. Spectral Analysis Results for a Variety of Temperature Time Series at Different Geographical Scales.

<i>Spatial Scale</i>	<i>Author (year)</i>	<i>Time Series</i>		<i>Significant Spectral Peaks Greater than 1 y</i>
		<i>Start Year</i>	<i>End Year</i>	
Global	Dehsara and Cehak [61]	1901	1960	None
Global Sea Surface	Folland et al. [62]	1856	1981	16y, 83y
Northern Hemisphere	Borzenkova et al. [63]	1881	1975	None
Central England	Shaw [64]	1659	1960	None
Central England	Shapiro [65]	1659	1973	2.1 y
Central England	Mason [41]	1700	1950	2.1 y, 5.2y, 7.6y, 14.5y, 23y, 76y
Central England	Plaut [42]	1659	1994	5.2y, 7.7y, 14.2y, 25y
Netherlands	Shaw [64]	1735	1944	None
Eastern North America	Mock and Hibler III [43]	1800	1975	20y
Albany, NY	Thaler [66]	1821	1983	None
New York City	Thaler [66]	1822	1983	None
		1822	1956	None
		1870	1959	50y

Table III. Spectral Analysis Results for a Variety of Precipitation Time Series.

<i>Spatial Scale</i>	<i>Author (year)</i>	<i>Time Series</i>		<i>Significant Spectral Peaks Greater than 1 y</i>
		<i>Start Year</i>	<i>End Year</i>	
England and Wales	Tabony [69]	1727	1975	2 y, 3.9 y
Kew, England	Tabony [69]	1697	1975	3.9 y, 6.1 y
Pode Hole, Lincolnshire, England	Tabony [69]	1726	1975	9.6 y
Manchester, England	Tabony [69]	1786	1975	3.9 y
Great Plains, US	Currie [70]	Unknown	Unknown	10 y, 18.6 y
US	Currie [70]	Unknown	Unknown	10 y, 18 y
Woodstock, MD, United States	Landsberg et al. [68]	1870	1959	None
South Africa	Burroughs [76]			3.5 y, 10-12 y, 18 y
South America	Burroughs [76]			3.8 y, 7 y, 20 y

over 1000 airports throughout the world [48,49]. The radiosonde network dates has a short duration, dating back to post World War II [50,51]. The shortest of these records make it almost impossible to assess the significance of any cycles in this data.

The quality and homogeneity of relative humidity times series have also been questioned. Atmospheric moisture measurements have been plagued by a numerous measurement problems like instrument inhomogeneities and non-standard reporting and analysis. For example, radiosonde instrument packages still differ from country to country and from manufacturer to manufacturer [50]. These differences make it difficult to compare site data, that is, the data are not homogeneous. Atmospheric moisture is also a difficult gas to measure since it does not mix well in the troposphere and it has a short atmospheric residence time (approximately 10 days) [52]. Thus, the amount of moisture in the air changes dramatically over the diurnal cycle [53]. Finally, atmospheric moisture measurements are reported in non-standard formats. For example, measurements are commonly reported as relative humidity, specific humidity, saturation deficit (the difference between the specific humidity at saturation and the measured specific humidity), and vertically integrated amount of water vapor. Non-standard formats make it difficult for the lay person to compare data from different monitoring stations.

Trend analysis results for atmospheric moisture are tabulated in Table 2.4. All trends for all regions are monotonically increasing for the entire measurement history for this weather element. No spectral analyses of atmospheric moisture has been found; this is probably due to the shortness of the time series for atmospheric moisture.

In conclusion, trend analysis and spectral analysis results for precipitation and atmospheric moisture exhibit high temporal and spatial variability, non-zero trends and few statistically significant cycles between 2 and 5 years. Thus, this moisture data provide little support for the premise that field exposure results are repeatable and reproducible.

Aerosols

Aerosols are suspensions of liquids or solids in a gas. Aerosols include a wide-range of particles like dust, smoke, haze, SO_x and NO_x having diameters in the range of 1 nm to 100 μm . Anthropogenic aerosols, especially SO_x and NO_x , have been implicated in the acid etching of organic coatings [54-57] and in the crazing of poly (methyl methacrylate) [58]. The contribution of aerosols to polymeric degradation, however, is the least understood of all of the weather elements.

Table 2.5 contains a selection of trends for SO_x , NO_x , fogs, and smoke at different geographical scales. Spectral analyses for aerosols were not located in the literature. From Table 2.5, trends for SO_x generally increased throughout the world until the mid-1960, with the exception of London, England. In the mid-1960's, Clean Air regulations were enacted in the United States and other industrial nations leading to a decreasing trend. For non-industrial regions of the world, the trends for both SO_x and NO_x are increasing over the entire measurement history.

Table IV . Trends in Relative Humidity Reported for Different Geographical Spatial Scales.

<i>Spatial Scale</i>	<i>Author (year)</i>	<i>Time Series</i>		<i>Moisture Content Variable</i>	<i>Trend Type (slope)</i>
		<i>Start Year</i>	<i>End Year</i>		
Northern Hemisphere	Salstein, Rosen, and Peixoto [49]	1958	1970	Vertical integrated amount of water vapor	↑
Equatorial Regions	Flohn and Kapala [71]	1949	1979	Saturation deficit	↑
Equatorial Regions --Americas and Africa	Hense et al [46]	1965	1984	Relative Humidity	↑
Equatorial Regions—Indo Pacific	Hense et al. [46]	1965	1984	Relative Humidity	↑
Equatorial Regions—Western Pacific	Gutzler [72]	1974	1988	Specific Humidity	↑

Figure V. Trend Analysis for Aerosols and Tropospheric Ozone Reported as
Increasing ↑, Decreasing ↓, or No-change →

	<i>Author (year)</i>	<i>Aerosol</i>	<i>Period 1</i>	<i>Period 2</i>	<i>Period 3</i>
Asia	Digano and Hameed [73]	SO _x		1880-1965 ↑	1965-1990 ↑
Europe	Digano and Hameed [73]	SO _x		1880-1965 ↑	1965-1990 →
North America	Digano and Hameed [73] and Karl et al. [74]	SO _x		1880-1965 ↑	1965-1990 ↓
Former USSR	Digano and Hameed [73]	SO _x		1880-1965 ↑	1965-1990 ↑
London	Brimblecomb et al. [75]	SO _x	1700-1830 →	1830-1900 ↑	1900-1990 ↓
London	Brimblecomb et al. [75]	Smoke	1700-1900 ↑	1900-1950 ↓	
London	Brimblecomb et al. [75]	Fog	1700-1830 →	1830-1900 ↑	1900-1950 ↓
London	Brimblecomb et al. [75]	NO _x			1976-1990 →

Summary

Field exposure results play a very important role in assessing the service life performance of polymeric materials. In particular, field exposure results are commonly viewed as the de facto standard of performance against which laboratory-aging experimental results must duplicate. As a standard of performance, field exposure results should be repeatable and reproducible. The literature was reviewed to find support either corroborating or refuting this repeatability and reproducibility premise.

Three sources of information were reviewed including testimonials from weathering researchers, results from well-designed and executed field exposure experiments, and trends and cycles in weather element data. Data from all three sources provided strong and consistent evidence refuting this premise and, correspondingly, provided little or no evidence corroborating the premise that field exposure results are either repeatable or reproducible.

All testimonials, except one, stated that field exposure results are neither repeatable nor reproducible for specimens exposed on different years, different times of the same year, for different exposure durations, for different exposure angles, or at different locations. Well-designed and executed field exposure experiments provided quantitative support for these claims indicating that exposure results could differ by as much as a factor of 10 for nominally identical specimens exposed on contiguous years at the same exposure site. The lack of reproducibility and repeatability of weathering results coincided with the lack of reproducibility and repeatability of all weather elements investigated. This later conclusion is consistent with conclusions from several recent studies [76-79]. Pittlock [80], for example, concluded that "most of the climatically important atmospheric and weather variables, be they temperatures, precipitation, or (say) ozone content, show day to day, seasonal, and year to year variations which are usually comparable with or larger than the variations in longer-term mean values".

Assuming that these conclusion are reaffirmed by other researchers, then the scientific validity of using field exposure results as the de facto standard of performance against which laboratory-aging results must duplicate must be questioned. It follows that service life prediction methodologies [81] that do not depend on field exposure results as a standard of performance should be more thoroughly investigated.

References

- 1 Clark, F.G., Industrial and Engineering Chemistry 1952; Vol. 44, p 2697.
Ellinger, M.L., Journal of Coatings Technology 1977; Vol. 49, p 44.

3. Boxall, J., *Journal of the Oil and Colour Chemists Association* 1986; Vol. 15, p 7.
4. Appleman, B.R., *Journal of Coating Technology* 1990; Vol. 62, p. 57.
Association of Automobile Industries, *Journal of Coatings Technology* 1986; Vol. 58, p. 57.
6. Martin, J.W., *Durability of Coatings and Plastics*, R.A. Ryntz [Ed.], Chapter 2, Hanser Publishers, New York, 2000.
7. Troutman, R.E.; Vannoy, W.G., *Journal of Industrial and Engineering Chemistry* 1940; Vol. 32, p 232.
8. Oakley, E., *Journal of the Oil Colour Chemists Association* 1960; Vol. 43, p 201.
9. Morse, M.P., *Official Digest* 1964; Vol. 36, p 695.
10. Mitton, P.B.; Church, R.L., *Journal of Paint Technology* 1964; Vol. 39, p 636.
11. Epple, R., *Journal of the Oil and Colour Chemist Association* 1968; Vol. 51, p 213.
12. Brighton, C.A., *Weathering and Degradation of Plastics*, Pinner, S.H. [Ed.], Columbine Press, London, 1966; p. 49
13. Ramsbottom, J.E., *Journal of the Royal Aeronautical Society* 1924; Vol. 28, p 273.
14. Ashman, G.W., *Journal of Industrial and Engineering Chemistry* 1936; Vol. 28, p 934.
15. Wirshing, R.J., *Journal of Industrial and Engineering Chemistry* 1941; Vol. 33, p 234.
16. Melchore, J.A., *Journal of Industrial and Engineering Chemistry: Product Research and Development* 1962; Vol. 1, p 232.
17. Joint Services Research and Development Committee on Paints and Varnishes, *Journal of the Oil and Colour Chemist Association* 1964; Vol 47, p. 73.
18. Singleton, R.W.; Kunkel, R.K.; Sprague, B.S., *Textile Research Journal* 1965; Vol. 35, p 228.
19. Clark, J.E.; Green, N.E.; Giesecke, P., *National Bureau of Standards Report, NBS Report 9912*, 1969.
20. Hoffmann, E.; Saracz, A., *Journal of the Oil and Colour Chemist Association* 1969, Vol 52, p 1130.
21. Fischer, R.M., *SAE Technical Paper Series 841022*, 1984.
22. Cleveland Society for Coatings Technology Technical Committee, *Journal of Coatings Technology* 1996; Vol. 68, p 47.
23. Marshall, J.; Iliff, J.W.; Young, H.R., *Journal of industrial and Engineering Chemistry* 1935; Vol. 27, p 147.
24. Qayyum, M.M.; Davis, A., *Polymer Degradation and Stabilization* 1984; Vol. 6, p 201.
25. Evans, P.D., *Polymer Degradation and Stabilization* 1989; Vol. 24, p 81.

26. Neville, G.H.J., *Journal of the Oil and Colour Chemists Association* 1963; Vol. 46, p. 753.
27. Scott, J.L., *Journal of the Oil Colour Chemists Association* 1983; Vol. 66, p 129.
28. Cutrone, L.; Moulton, D.V., *Journal of the Oil and Colour Chemist Association* 1987; Vol. 70, p 225.
29. Dawson, D.H.; Nutting, R.D., *Journal of Industrial and Engineering Chemistry* 1940; Vol. 32, p 112.
30. Came, C.L., *Journal of Research of the Bureau of Standards* 1930; Vol. 4, p 247.
31. Lehmann, D.E., *Non Parametrics: Statistical Methods Based on Ranks*, Holden-Day, New York, 1978.
32. National Bureau of Standards, *National Bureau of Standards Circular* 505, 1951.
33. Ultraviolet Radiation Panel, *United States Global Change Research Program Publication USGCP-95-01*, 1995.
34. Weatherhead, E.C.; Webb, A.R., *Radiation Protection Dosimetry* 1997; Vol. 72, p 223.
35. Subcommittee on Global Change Research, *National Science and Technology Council Annual Report*, Washington, D.C., 1998.
36. Scotto, J.G.; Cotton, G.; Urbach, F.; Berger, D.; Fears, T., *Science* 1988; Vol. 239, p 762.
37. Correll, D.L.; Clark, C.O.; Goldberg, B.; Goodrich, V.R.; Hayes, D.R.; Klein, W.H.; Schecher, W.D., *Journal of Geophysical Research* 1992; Vol. 97(D7), p 7579.
38. McKenzie, R.; Connor, B.; Bodeker, G., *Science* 1999; Vol. 285, p 1709.
39. Kerr, J.B.; McElroy, C.T., *Science* 1993; Vol. 262, p. 1032.
40. Jones, P.D.; Hulme, M., *Climates of the British Isles: Present, Past, and Future*, Hulme, M. and Barrow, E. [Eds.], 1997; p. 173
41. Mason, B.J., *Quarterly Journal of the Royal Meteorological Society*, 1976; Vol. 102, p 473.
42. Plaut, G.; Ghil, M.; Vautard, R., *Science* 1995; Vol. 268, p 710.
43. Mock, S.J.; Hibler III, W.D., *Nature* 1976; Vol. 261, p 484.
44. Coleman, B.D., *Journal of Applied Physics* 1956; Vol. 27, p 862.
45. Bradley, R.S.; Diaz, H.F.; Eischeid, J.K.; Jones, P.D.; Kelly, P.M.; Goodess, C.M., *Science* 1987; Vol. 237, p 171.
46. Hense, A.; Krabe, P.; Flohn, H., *Meteorology and Atmospheric Physics* 1988; Vol. 38, p 215.
47. Groisman, P. Ya, *Greenhouse-Gas-Induced Climate Change: A Critical Appraisal of Simulations and Observations*, Schlesinger, M.E. [Ed.], Elsevier, New York, 1991; p. 297

48. Peixóto, J.P. ; Oort, A.H., *Variations in the Global Water Budget*, Street-Perrott, A, Beran, M., and Ratcliffe, R. [Eds.], D. Reidel Publishing Company, Boston, 1982; p 5.
49. Salstein, D.A.; Rosen, R.D.; Peixoto, J.P., *Journal of the Atmospheric Sciences* 1983; Vol 40, p 788.
50. Gaffen, D.J.; Barnett, T.P.; Elliott, W.P., *Journal of Climate* 1991; Vol. 4, p 989.
51. Peixóto, J.P.; Oort, A.H. *Physics of Climate*, American Institute of Physics, New York, 1992.
52. Elliott, W.P.; Smith, M.E.; Angell, J.K., *Greenhouse-Gas-Induced Climatic Change: A Critical Appraisal of Simulations and Observations*, Schlesinger, M.E. [Ed.], Elsevier, New York, 1991; p 311
53. Rasmusson, E.M., *Water Resource Research* 1966; Vol. 2, p 469.
54. Wolff, G.T.; Rodgers, W.R.; Collins, D.C.; Verma, M.H.; Wong, C.A., *Journal of Air and Waste Management Association* 1990; Vol 40, p 1638.
55. Schulz, U.; Trubiroha, P., *Durability Testing of Non-Metallic Materials*, ASTM STP 1294, R.J. Herling [Ed.], American Society for testing and Materials, Philadelphia, 1996.
56. Wernstahl, K.M.; Carlsson, B., *Journal of Coatings Technology* 1997; Vol. 69, p 69.
57. Rodgers, W.R.; Garner, D.P.; Cheever, G.D., *Journal of Coatings Technology* 1998; Vol. 70, p. 83.
58. Schulz, U.; Trubiroha, P.; Boettger, T.; Bolte, H., *Proceedings of the 8th International Conference on Durability of Building Materials and Components*, meeting held in Vancouver, B.C. from May 30 to June 3, 1999, NRC Research Press, Ottawa, Canada, 1999; p. 864.
59. Jones, P.D., *World Survey of Climatology: Future Climates of the World: A Modelling Perspective* , H.E. Landsberg [Ed.], Elsevier, New York, 1995; p. 151.
60. Diaz, H.F.; Bradley, R.S., *Natural Climatic Variability on Decade-to-Century Time Scales*, Climate Research Committee, National Academy Press, Washington, D.C., 1995; p 17.
61. Dehsara, M.; Cehak, K., *Arch. Meteorolog. Geophysics Bioklimatol. Soc. Series B*, 1970; Vol 19, p 269.
62. Folland, C.K.; Parker, D.E.; Kates, F.E., *Nature* 1984; Vol. 310, p 670.
63. Borzenkova, I.I.; Vinnikov, K. Ya.; Spirina, L.P.; Stechnovsky, D.I., *Meteorol. Gidrol. No. 7*, 1976; p 27.
64. Shaw, D., *Journal of Geophysical Research* 1965; Vol. 70, p 4997.
65. Shapiro, R., *Quarterly Journal of the Royal Meteorological Society* 1975; Vol. 101, p 679.

66. Thaler, J.S., *Climate: History, Periodicity, and Predictability*, Rampino, M.R., Sanders, J.E., Newman, W.S., and Königsson, L.K [Eds.], Van Nostrand Reinhold, 1987.
67. Spar, J.; Mayer, J.A., *Weatherwise* 1973; Vol. 26, p 128.
68. Landsberg, H.E.; Mitchell, J.; Crutcher, H., *Monthly Weather Review* 1959; Vol. 87, p 283.
69. Tabony, R.C., *The Meteorological Magazine* 1979; Vol. 108, p 97.
70. Currie, R.G., *Climate: History, Periodicity, and Predictability*, Rampino, M.R., Sanders, J.E., Newman, W.S., and Königsson, L.K [Eds.], Van Nostrand Reinhold, 1987.
71. Flohn, H.; Kapala, A., *Nature*, 1989; Vol. 338, p 244.
72. Gutzler, D.S., *Geophysical Research Letters* 1992; Vol. 19, p 1595.
73. Dignon, J.; Hameed, S., *Journal of Air Pollution Control Association* 1989; Vol. 39, p 180.
74. Karl, T.R.; Jones, P.D.; Knight, R.W.; Kukla, G.; Plummer, N.; Razuvayev, V.; Gallo, K.P.; Lindesay, J.A.; Charlson, R.J., *Natural Climate Variability on Decade-to-Century Time Scales*, Climate Research Committee of the National Research Council, National Academy Press, Washington, D.C., 1995; p. 80.
Brimblecombe, P.; Benthon, G., *Climates of the British Isles: Present, Past, and Future*, Hulme, M. and Barrow, E. [Eds.], Routledge, 1997; p. 243.
76. Burroughs, W.J., *Weather Cycles Real or Imagery?*, Cambridge University Press, New York, 1992. .
Climate Research Committee, *Natural Climate Variability on Decade-to-Century Time Scales*, National Academy Press, Washington, D.C., 1995.
78. National Research Council, *Decade-to-Century-Scale Climate Variability and Change*, National Academy Press, Washington, D.C., 1998.
79. Von Storch, H.; Navarra, A.[Eds.], *Analysis of Climate Variability*, Springer, New York, 1999.
80. Pittock, A.B., *Review of Geophysical Space Physics* 1978; Vol. 16, p 400.
81. Martin, J.W.; Saunders, S.C.; Floyd, F.L.; Wineburg, J.P., *Federation Series on Coatings Technology, Federation of Societies for Coatings Technology*, Blue Bell, PA, 1996.